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EVALUATION OF SINGLE-PASS SEAWATER REVERSE OSMOSIS MODULES AND --ETC(U)

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**DAVID W. TAYLOR NAVAL SHIP  
RESEARCH AND DEVELOPMENT CENTER**

Bethesda, Md. 20084



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**EVALUATION OF SINGLE PASS SEAWATER REVERSE  
OSMOSIS MODULES AND PRETREATMENT TECHNIQUES**

By  
J. F. Pizzino



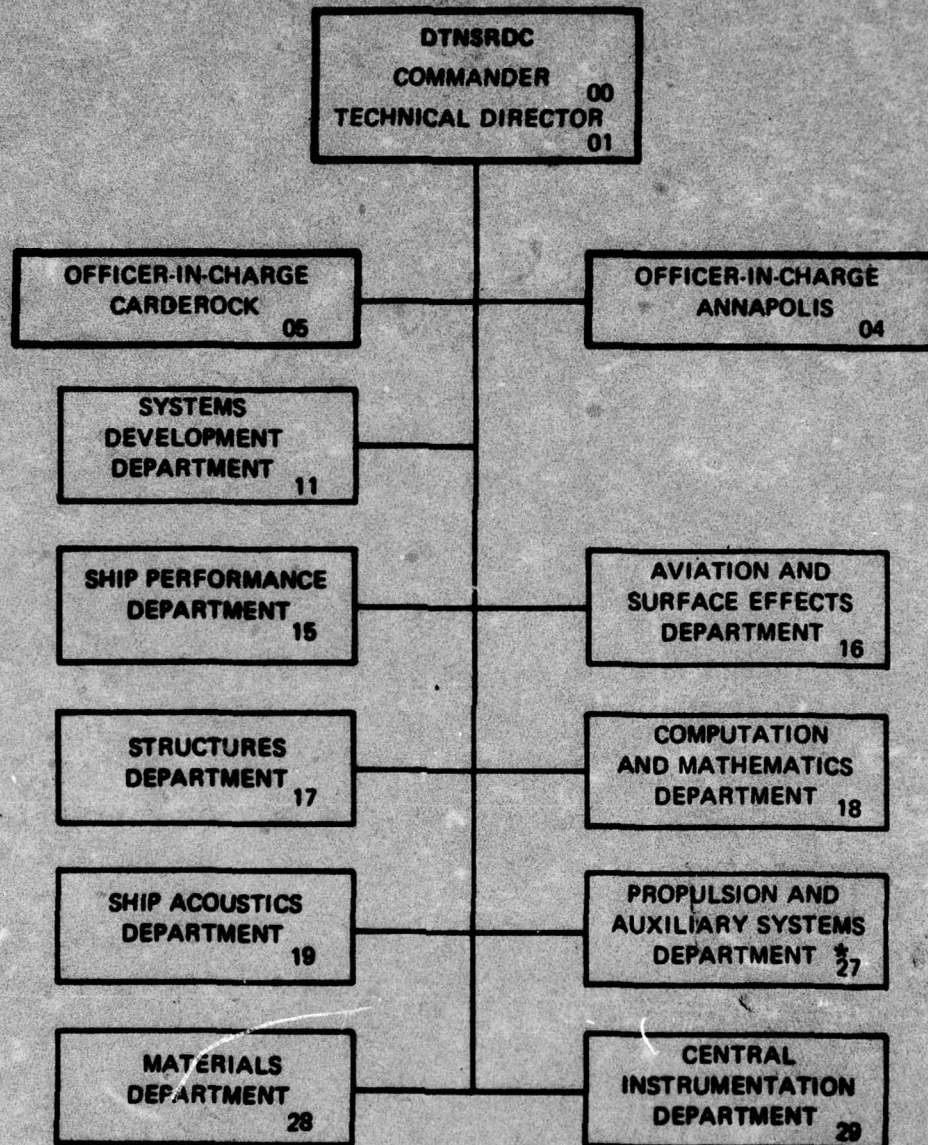
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**PROPULSION AND AUXILIARY SYSTEMS DEPARTMENT  
ANNAPOLIS  
RESEARCH AND DEVELOPMENT REPORT**

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Report 78-0121

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hours of operation after 3800 total operating hours. Permeate total dissolved solids for all modules were consistently less than 500 parts per million. It was found that a high degree of filtration was necessary for the successful operation of reverse osmosis modules for seawater desalination. The use of electrolytically generated chlorine to prevent membrane biological attack (and/or fouling) and to produce chlorinated potable water without the use of any chlorine compounds was considered very successful.

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## ACKNOWLEDGMENTS

The author would like to express his appreciation to Mr. Dean Ammons of Dow Chemical Company for his technical advice during the course of these evaluations, and also to Mr. Jesse Garriss of the Francis L. LaQue Corrosion Laboratory, Wrightsville Beach, North Carolina, for his assistance in the operation and maintenance of the test systems.

## LIST OF ABBREVIATIONS

atm	- atmospheres
gpd	- gallon per day
hr	- hour
°F	- degree Fahrenheit
°K	- degree Kelvin
lpd	- liter per day
μm	- micrometer
PI	- plugging index
ppm	- part per million
PR	- permeate (product) rate
psig	- pounds per square inch gage
RO	- reverse osmosis
TDS	- total dissolved solids
UF	- ultrafiltration
mm	- millimeter
gpm	- gallon per minute



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## ABSTRACT

Four reverse osmosis modules were evaluated on natural seawater at Wrightsville Beach, North Carolina. Three of the modules were run on chlorinated and cartridge filtered seawater, and all showed permeate rate declines greater than 30% per thousand hours. The fourth module, run on chlorinated, ultrafiltered seawater feed showed an average permeate rate decline of 4.7% per thousand hours of operation after 3800 total operating hours. Permeate total dissolved solids for all modules were consistently less than 500 parts per million. It was found that a high degree of filtration was necessary for the successful operation of reverse osmosis modules for seawater desalination. The use of electrolytically generated chlorine to prevent membrane biological attack (and/or fouling) and to produce chlorinated potable water without the use of any chlorine compounds was considered very successful.

## INTRODUCTION

### BACKGROUND

Reverse osmosis desalination is a process by which high-pressure saline water is forced through a semipermeable membrane to produce potable water. The Center has been developing the RO\* process for shipboard desalination. The major advantage of this technique is the large potential for saving energy (75%-80%) compared to conventional shipboard distillation systems. Other potential advantages include reduced weight and volume, lower maintenance requirements, safer operation, and the ability to provide chlorinated potable water without the use of dangerous chlorine compounds.

Initially, two cellulose triacetate hollow fiber RO modules were evaluated, one on synthetic seawater at this Center and the other on natural seawater at the Francis L. LaQue Corrosion Laboratory, Wrightsville Beach, North Carolina.<sup>1</sup> These tests were conducted to determine membrane performance and possible problem areas. The two problem areas identified were membrane fouling by iron oxides and biological attack of the membrane.

\*Definitions of abbreviations appear on page i.

<sup>1</sup>Superscript refers to similarly numbered entries in the Technical References at the end of the text.



Membrane fouling resulted in a PR decline accompanied by some decline in salt rejection. Bacterial attack caused a precipitous loss in salt rejection.

The purpose of the investigation reported herein was to develop a single-pass RO seawater desalination system to provide freshwater for nonsteam powered surface ship requirements.

## SCOPE

This report details results of the 400-gpd (1512-lpd) seawater RO pilot plant evaluation and the methods used to pretreat the seawater prior to the RO process. A 400-gpd seawater desalination plant was procured for testing on natural seawater. Steps were taken to reduce the causes of failure experienced in earlier tests. To reduce the possibility of iron fouling, type 316 stainless steel and copper alloys were used exclusively in the system fabrication. To prevent biological attack, the injection into the feed seawater stream of a sodium hypochlorite solution and later electrolytically generated chlorine solutions were employed. Ultrafiltration was employed and tested as a method of filtering the seawater feed to remove particulate matter.

## METHOD OF EVALUATION

Item (a), figure 1, illustrates the pretreatment scheme used during the initial phase of the 400-gpd RO system. Seawater was first passed through a settling and deaeration tank and was followed by injection of 0.2 ppm sodium hypochlorite solution. Seawater was then fed to 5.0 and 1.0  $\mu$ m in-depth type cartridge filters and then through an ultraviolet-light water sterilizer.

Figure 2 gives a front and rear view of the 400-gpd RO seawater system; item (a), figure 3, provides a piping schematic of the RO system. The low-pressure pretreated seawater was pumped to 800 psig (55.4 atm) with a single cylinder diaphragm pump and then supplied to the two RO modules piped in parallel. Any excess seawater was bypassed through a back-pressure valve to drain. Permeate (RO product water) flow rate and electrical conductivity were continually monitored. The seawater brine (concentrate) flow rate was set at the desired level with flow control valves located at the discharge from the modules. Brine flow rate was monitored with rotameters.

The addition of chlorine was intended to control bacteriological activity, a problem encountered in earlier work. An ultraviolet-light water purifier was also included to supplement

chlorination to control bacteriological activity. Monel components were installed where possible to reduce iron oxide membrane fouling; otherwise, type 316 stainless steel parts were used.

During the evaluation of the above system, it became evident that modifications were necessary to continue the tests and improve performance. The high-pressure pump initially provided with the system failed due to overstress in certain key components. To continue the evaluation with minimum delay, a readily available, smaller capacity pump was substituted. This limited the evaluation to the testing of one 200-gpd (756-lpd) RO module rather than the original two modules.

It was also evident that an improved method of filtration was required to obtain good results with the RO system. Therefore, a UF system was installed as part of the pretreatment process.

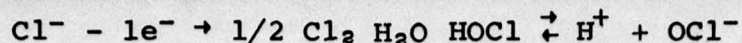
Item (b), figure 1, illustrates the key components in the operation of the modified 200-gpd system. Seawater from the deaeration tank was pumped through the UF system. Chlorine was injected into the UF permeate. This chlorinated feed was passed through an ultraviolet purification unit and then pumped into the RO unit. The 200-gpd RO unit, shown schematically in item (b), figure 3, was operated in a manner essentially identical with the 400-gpd unit except for a different pump and the use of one RO module rather than two.

A more detailed description of the UF pretreatment system and results of tests on that system may be found in appendix A.

During the initial evaluation of the 400-gpd unit, it was found that a large amount of copper salts were leaching from the Monel piping and collecting on the RO membrane fibers. All Monel parts were subsequently replaced with type 316 stainless steel parts.

When the 200-gpd system (item (b), figure 1) was run for almost 3000 hours, it was noted that a large amount of iron oxide from the seawater precipitated in the holding tank downstream of the UF modules. This precipitation was thought to be a result of the oxidation of iron in the seawater from the chlorination process. Therefore, the chlorinator was moved upstream of the UF system so that iron oxide precipitation would occur prior to UF. In place of the sodium hypochlorite solution-injection chlorination system, an electrolytic chlorine generator was substituted. This chlorinator transforms chloride ions into free chlorine by the following chain reaction:





by this method the seawater was chlorinated without the normally required addition of chlorine compounds.

In addition, a chlorine-sensing instrument which continuously measures hypochlorous acid (HOCl) by the use of a polarographic membrane electrode was added to the test system. The results with the chlorine probe as a measuring device are described in appendix B. Item (c), figure 1, details the components in the second modification to the original system.

## DESCRIPTION OF REVERSE OSMOSIS MODULES

The basic design of the hollow fiber RO module is shown in figure 4. Water flows into the slotted PVC core and flows out radially through the fiber bundle. As it passes through the bundle some water permeates the hollow fiber walls and flows through the hollow channel to the permeate channel where it is collected before exiting the module. Feedwater that does not permeate the fibers (brine or seawater concentrate) exits the module through a port at the hemispherical end of the pressure vessel.

## TARGET GOALS

For the evaluation of RO modules, two criteria were established to judge the success of the evaluation. First, RO permeate had to have less than 500 ppm TDS. Secondly, the permeate rate decline of a given RO module had to be less than 10% over a 1000-hour operating period. The first objective had been achieved in previous work<sup>1</sup> with similar cellulose triacetate hollow fiber modules; however, the second objective was not attained in the earlier studies.

These two target goals have carried the added stipulation that no acid addition be required for their attainment. Most RO equipment manufacturers and investigators have used acid addition in their installations to maintain a pH range of 5 to 7 to reduce the membrane hydrolysis rate and increase the solubility of ionic species (such as iron) that would otherwise tend to foul the membrane. The avoidance of acidification for pH control in earlier tests had undoubtedly contributed to the difficulties in attaining the second objective. However, the carrying of acid is considered to be a major safety and logistics problem that should be avoided in the design of such a system, if at all possible.

The main thrust of the present program was to investigate methods of pretreating seawater so that product rate declines could be minimized. The goal of avoiding acid pretreatment remained in effect.

## BIOLOGICAL ANALYSES

Biological analyses were made by the spread plate method.<sup>2</sup> Originally, the purpose of these analyses was to obtain a qualitative knowledge of the various streams going to and from the RO module. Also, in case of a module failure, this information would aid in the determination of the cause of such a failure.

## PLUGGING INDEX

During previous investigations of RO modules, the need to describe the level of particulates in RO feedwater that can adversely affect the performance of RO modules became apparent. A method<sup>3</sup> has been developed which quickly gives a measure of the potential of RO feedwater to foul a hollow fiber RO module. This procedure involves measuring the flux decline of a 0.45  $\mu$ m laboratory filter pad that is fed with RO feedwater at 30 psig (2.04 atm).

In the evaluations of modules A, B, and C, 5-minute plugging indexes ( $PI_5$ ) were used. This plugging index provides the percent filter pad flux decline over a 5-minute interval; the value thus obtained is divided by five to give a  $PI_5$  value. In taking data, it was later found that measuring the percentage flux decline over a 15-minute interval and dividing by 15 to obtain a 15-minute plugging index ( $PI_{15}$ ) was more repeatable. The  $PI_{15}$  test was used in testing module D. Generally  $PI_5$  and  $PI_{15}$  values for RO feedwater of less than 6 and 3.3, respectively, were recommended by the manufacturer of the hollow-fiber RO module.

## RESULTS AND DISCUSSION

### INITIAL EVALUATION OF 400-GALLON-PER-DAY UNIT

Items (a), (b), and (c), figure 5, give the results of the three RO modules evaluated on chlorinated, cartridge-filtered seawater feed. Each data point indicates an actual reading of PR and permeate quality taken at the indicated operating hour. Initially, modules A and C were tested with the piping configuration shown in item (a), figure 3. Module A was replaced after approximately 500 hours by module B because its performance had declined to a point where its product TDS level had risen above the maximum allowable level of 500 ppm.

As can be seen from items (a), (b), and (c), figure 5, permeate water TDS remained below the maximum limit of 500 ppm in most cases. However, as in previous testing,<sup>1</sup> flux declines



were excessive. Percentage flux declines per thousand operating hours for modules A, B, and C were 48%, 40%, and 33%, respectively.

The poor PR performance did not appear to be a result of biological causes since permeate water quality was generally stable and biological analyses did not indicate an abrupt increase in biological activity during the test. The decline appeared to be directly related to the poor filtration obtained with the cartridge filters. During the tests on modules A, B, and C feedwater  $PI_{15}$  values varied widely over a range of 5 to 15, many of which values were above the desired maximum of 6.0.

The apparent loss in salt rejection of module A was believed to have been caused by channeling effects resulting from particulate fouling.

With all of the modules investigated, free chlorine was not rejected by the RO membrane to an appreciable degree. Feedwater chlorine levels of 0.2 ppm were maintained throughout the duration of the evaluation of the above three RO modules.

#### MODIFIED 200-GALLON-PER-DAY UNIT

Figure 6 shows the results of RO module D run on chlorinated and ultrafiltered seawater for 3800 hours. Each data point represents an average weekly value. The uppermost set of points indicates the permeate water quality; the middle set of points gives the  $PI_{15}$  value of the RO feedwater while the lowest points give PR values.

This evaluation was separated into several interconnected phases. From 0 to 2050 hours, the system was run in the normal fashion for 24 hours a day with the chemical injection chlorinator operating continuously. From 2050 to 3500 hours chlorination was limited to 8 hours a day only. This latter method of chlorination was intended to establish whether chlorination could be used intermittently and still be effective in preserving the membrane from biological attack. At 2900 hours the original liquid injection type chlorinator was replaced by an electrolytic type chlorinator installed upstream of the UF system.

As can be seen, the overall average flux decline was 4.7% per 1000 hours of operating time - well within the desired target value of 10%. Also, during the evaluation, salt rejection declined slightly but never to an unacceptable level.

During the first period, from 0-2050 hours, the PR decline per 1000 hours was approximately 10%.  $PI_{15}$  values during that

period sometimes increased above the desired maximum value of 3.3. It is interesting to note that PR data points between 1000 and 2000 hours show a stronger decline than those points between 0 and 1000 hours. Corresponding  $PI_{15}$  values between 600 and 900 hours indicate that the RO module had been exposed to a poor quality (i.e., high particulate) feedwater during that time. The PR data indicated that even though a high quality feed was provided after 900 hours, the initial exposure to the lower quality feedwater did have a delayed effect on the RO performance as the increased PR decline after 1000 hours indicates.

During the second period of performance, from 2050 to 2700 hours, the RO performance stabilized, apparently due to the continued use of high quality feedwater (as seen in  $PI_{15}$  values) up to 2500 hours of operation. It appears that intermittent use of the chlorinator during this period did not adversely affect system performance. Whether this could be attributed to the continuous use of the ultraviolet-water purifier was not determined. It is believed, however, that this device may have played a role in bacterial control.

At 2900 hours when the liquid-injection chlorinator was replaced by the electrolytic chlorinator, a strong PR decline was seen. It is believed that this PR decline was not caused by the introduction of electrolytically generated chlorine, but by another decline in feedwater quality ( $PI_{15} < 3.3$ ) which again resulted in a subsequent PR decline (2700 to 3500 hours).

To show that the electrolytic chlorinator was, in fact, not responsible for the strong PR decline experienced during that period, the RO module was cleaned by a previously developed cleaning solution<sup>4</sup> and the electrolytic chlorinator was run full-time starting at 3500 hours. A new UF cartridge was installed in the UF system to provide higher quality feedwater. As can be seen from figure 6, the PR was partially restored as a result of the cleaning solution and no substantial PR decline followed. The ingredients for the solution which proved to be very effective are:

Water	97.0%
Sodium EDTA	0.9%
Triton X-100	0.1%
Sodium Phosphate	2.0%

During the entire length of this evaluation there again was no evidence of chlorine rejection by the RO module. Biological analyses taken during the duration of the evaluation indicated that the chlorine level used (0.2 to 0.5 ppm) was adequate in reducing the generally high level of organisms in the seawater.



Moreover, no abrupt biological changes in any of the chlorinated streams appeared.

During the duration of the evaluation, permeate quality varied from 100 to 250 ppm TDS. Even when the RO module was cleaned at 3500 hours, no appreciable improvement in permeate quality resulted. This gradual permeate quality decline is believed to be caused by gradual membrane hydrolysis, which was accelerated by the high seawater pH levels (7.8-8.2). Other investigators have lowered seawater pH levels with acid to reduce this hydrolysis; however, logistically this is considered undesirable for shipboard systems if it can be avoided. The vendor of the RO module is currently working on the approval by the Federal Food and Drug Administration of an additive that, when fed to an RO module, acts to tighten and therefore improve the membrane rejection after a decline in salt rejection has occurred.

### CONCLUSIONS

In the evaluation described herein, several conclusions can be drawn. First and most evident, for successful RO operation, a higher degree of prefiltering is required than that provided by conventional, in-depth, cartridge filtration. In the evaluation of modules A, B, and C with in-depth, cartridge-type filtration,  $PI_s$  values were erratic and uncontrollable, which caused serious flux declines. In the evaluation of module D, (where UF was used for pretreatment) in the two cases where PR declines were large, it was found that the  $PI_s$  values had previously increased to above 3.3 for some period of time. The use of UF for the pretreatment was generally successful in producing seawater of suitable purity for supply to the RO unit.

Also, the use of chlorine with cellulose triacetate membranes appears to be a successful method of ensuring against membrane attack by biological agents and for producing chlorinated permeate. These data from module D indicate that chlorination is not necessary for the entire period of RO operation to be successful. Whether this could be attributed to the supplementation of the ultraviolet-water purifier was not determined.

The use of the electrolytic chlorine generator showed that it was possible to produce chlorinated RO permeate without the use of chemicals. In addition, successful operation was realized without the use of acid addition.

The use of a special membrane cleaning solution was considered effective in restoring much of the permeate rate lost due to membrane fouling.

The present limit on the operating life of the RO module, as long as feedwater is always of acceptable quality, appears to be related to a loss of salt rejection from membrane hydrolysis effects and irreversible flux reductions due to membrane compaction. Two methods for substantially reducing these losses and extending membrane life are:

- The use of the previously mentioned membrane coating and cleaning solutions.

- Acidification of the feedwater to reduce hydrolysis effects (if this is deemed logistically acceptable for ship use).

These developments can, therefore, increase the life expectancy of the RO module.

It appears from the data obtained for module D that a significant improvement in membrane performance has been achieved over a previous testing. On the basis of this performance the RO system is considered to be suitable for ship operation. However, the UF system which was used to produce the high purity feedwater is considered somewhat marginal. During 3800 hours of testing, the UF module had to be replaced twice. Initial results using diatomaceous earth filtration have been very encouraging and it appears to be a more likely candidate for a shipboard RO pretreatment system unless UF module life can be improved.

#### FUTURE PLANS

Future plans include testing the RO system with a diatomaceous earth filter in place of the UF system, since the lifetime of the latter method up to this point is not considered acceptable for ship application. Tests are now underway on the diatomaceous earth filter, and a report of these results, which look very promising, will be available shortly. As part of these tests, in-depth quantitative biological analyses are being made to certify the fitness of the RO permeate for human consumption aboard ship.

#### TECHNICAL REFERENCES

- 1 - Pizzino, J. F. and W. L. Adamson, "Evaluation of Seawater Reverse Osmosis Modules for Single-Pass Shipboard Desalination Systems," NSRDC Rept 27-717 (Mar 1974)
- 2 - Heeb, Mary Jo and M. E. Atkins, OSW Laboratory Test OSW-73-01 (23 Jan 1973)
- 3 - "Standard Millipore Test for Determining Fouling Characteristics of Permeator Feed Supply," Tech Bull. 300, E.I. DuPont De Nemours & Co., Inc., Permasep Products, Wilmington, Dela.



4 - Bevedge, E., et. al, "Interaction of Feedwater Colloids with the Surface of RO Membranes," OSW Contract 14-30-80 (

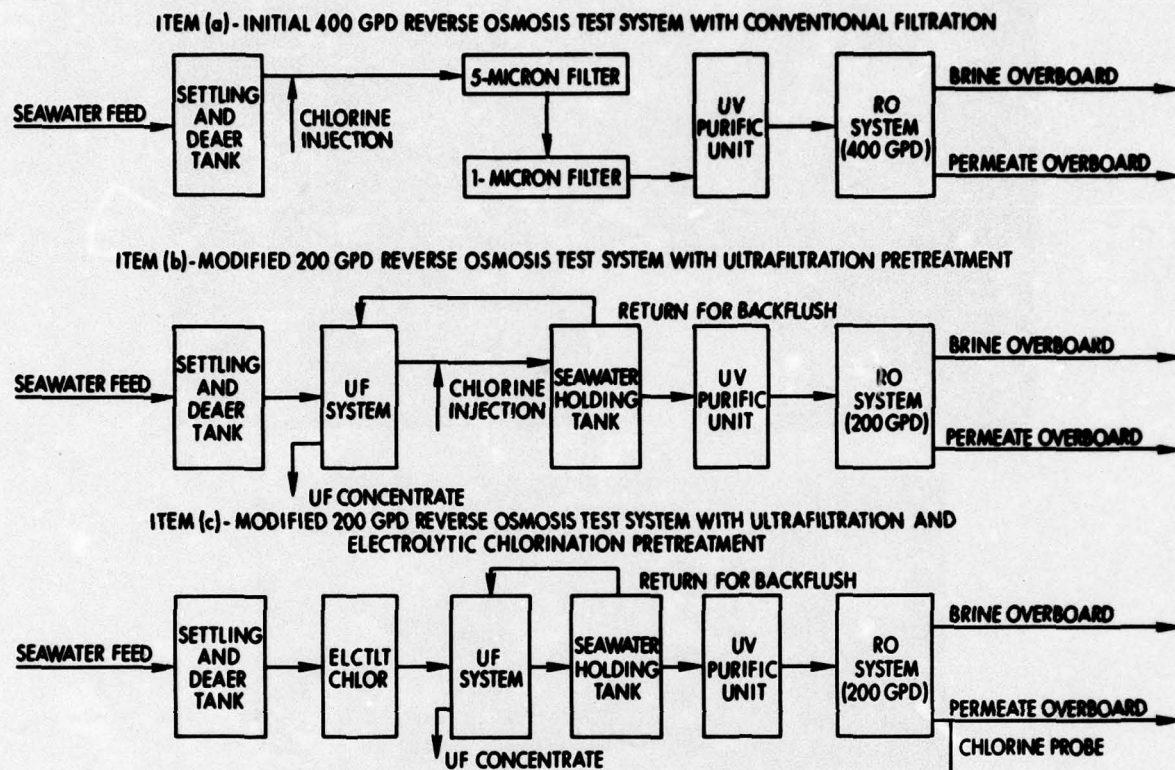


Figure 1  
Reverse Osmosis Test Systems



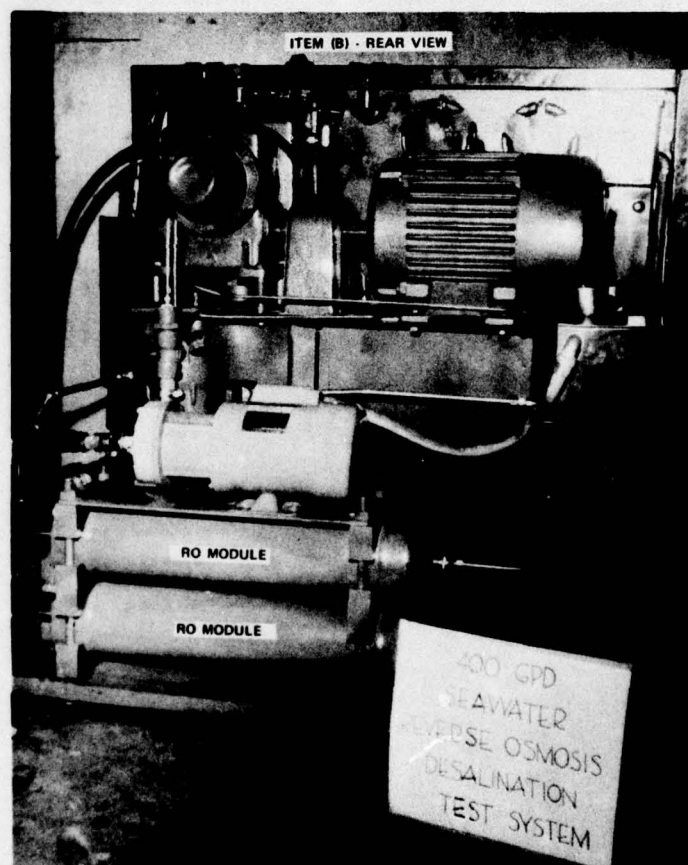
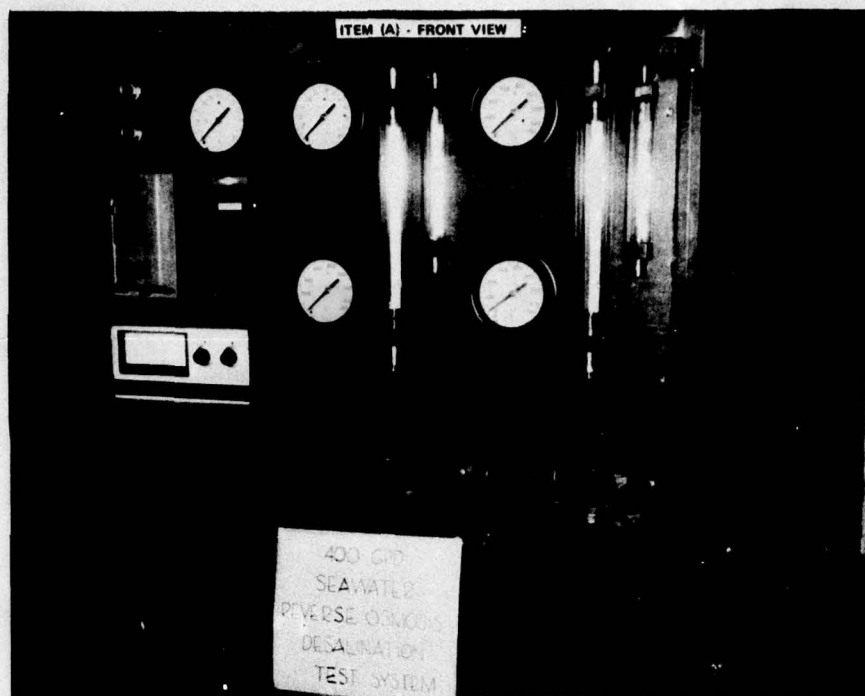


Figure 2  
400-GPD Reverse Osmosis Desalination Unit

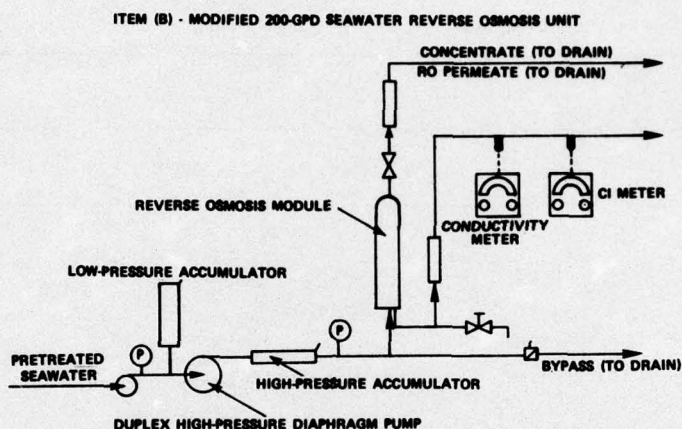
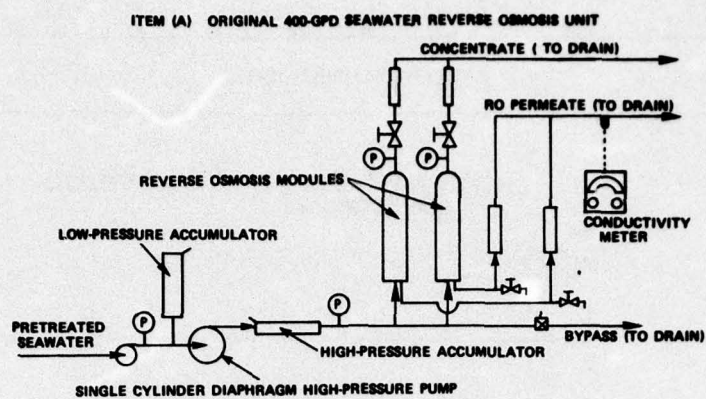


Figure 3  
Reverse Osmosis Seawater Desalination  
System Flow Schematics

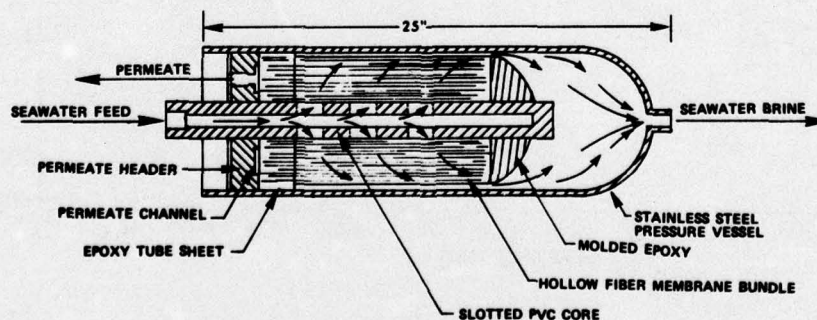


Figure 4  
Hollow Fiber Seawater Reverse Osmosis Module



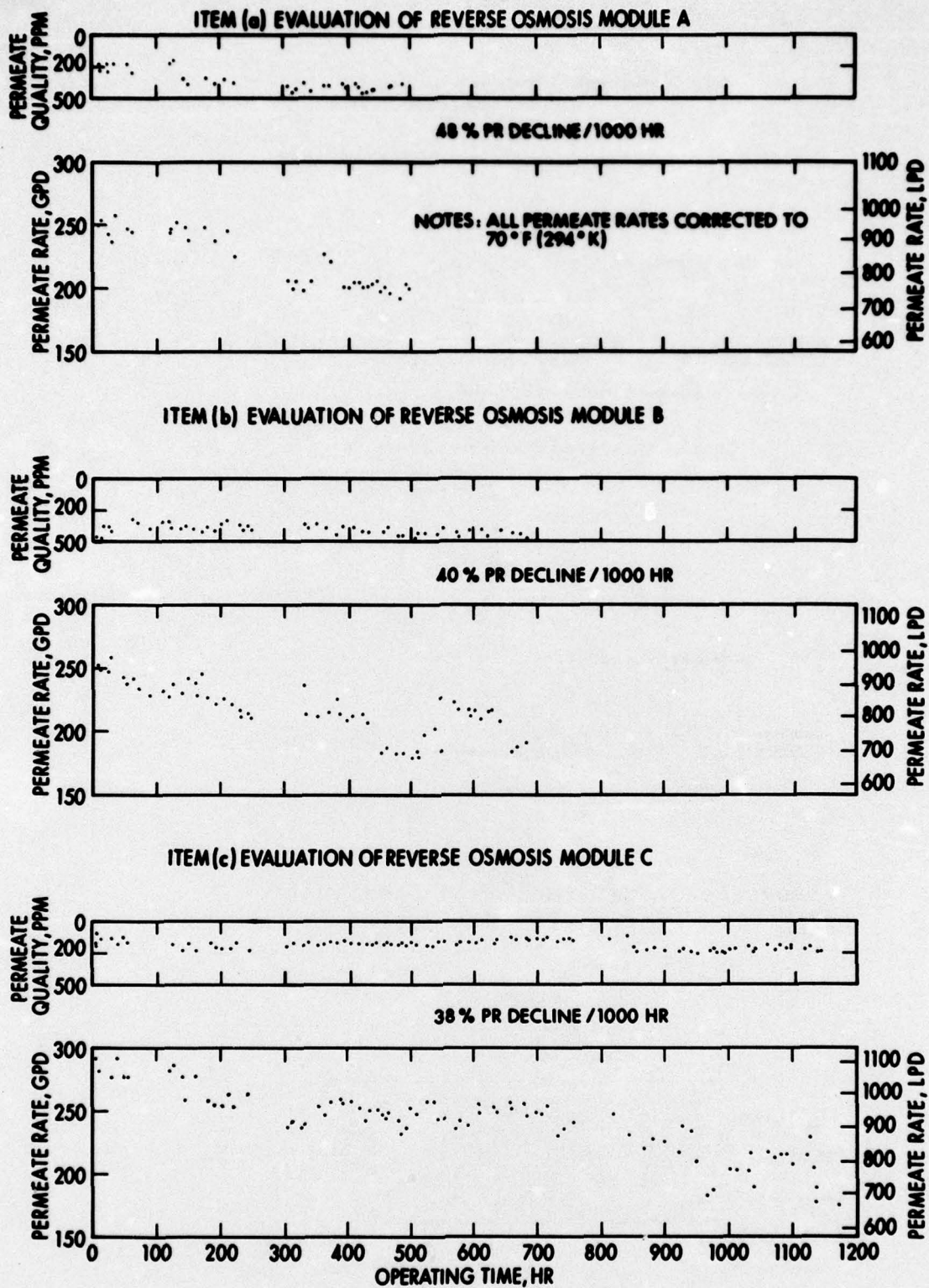


Figure 5  
Results of Three Reverse Osmosis Modules  
Evaluated in a Seawater Reverse Osmosis System

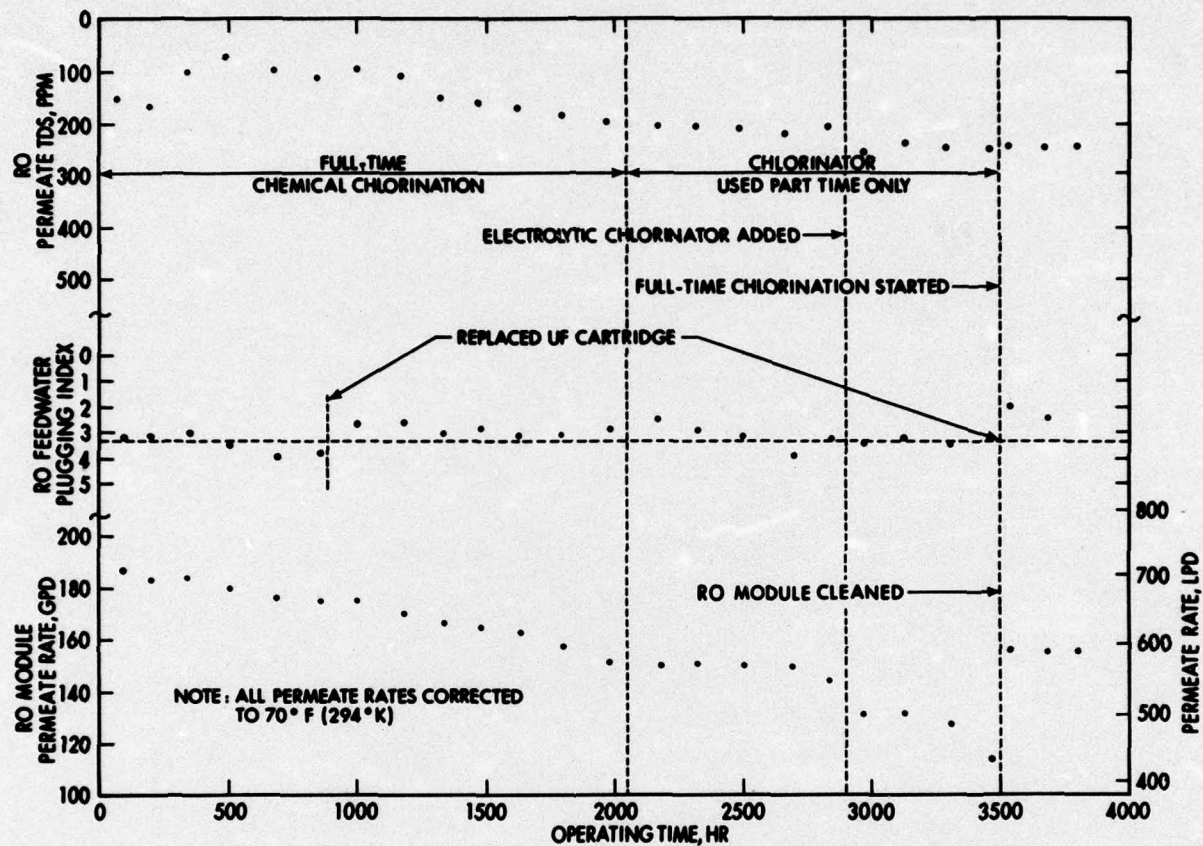


Figure 6  
Results of Seawater Reverse Osmosis Test  
System Operated on Ultrafiltered Seawater Feed



APPENDIX A  
ULTRAFILTRATION FOR PRETREATMENT OF SEAWATER

During the evaluation of the original 400-gpd seawater RO system it became evident that a high degree of filtration of seawater was necessary for the prevention of fouling of the RO membrane. For this reason UF was evaluated and used in the modified 200-gpd test system. The effectiveness of this method was determined by plotting  $PI_{15}$  values and UF permeate rates with operating time.

A commercially available UF membrane module was selected for this application. Figures 1-A and 2-A are photographs of the module. The module is designed in a fashion similar to a heat exchanger. The membranes are hollow tubular structures (0.50 mm inner diameter) which are embedded in an epoxy tube sheet at each end of the module. Feedwater flows through the inside of the tubes while UF permeate passes through the porous tube walls and is collected on the shell side. This module can be backflushed to force UF permeate back through the tubular membrane from the shell to the tube side and thereby dislodge foulant particles.



Figure 1-A  
End View of Ultrafiltration Cartridge

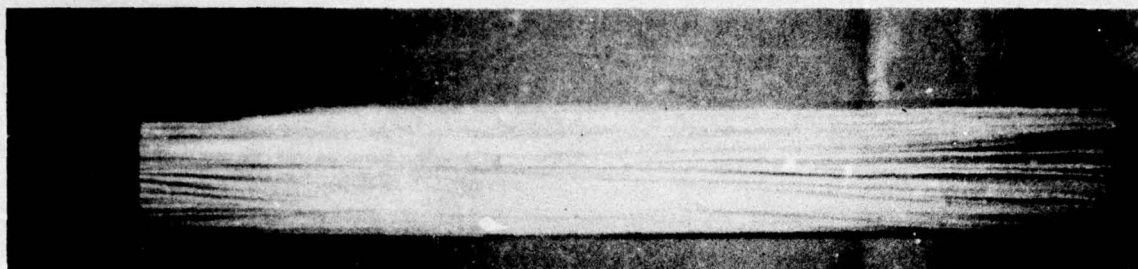


Figure 2-A  
Front View of Ultrafiltration Cartridge

A schematic of the UF system is shown in figure 3-A. Cartridge filtered (125  $\mu$ m) seawater was provided to the UF cartridge. A part of the concentrate stream was bled off with a needle valve. The remainder was fed back to the recirculation pump suction. Recirculation flow was adjusted to obtain 6 gpm to the UF module. This flow corresponded to a Reynolds number in the tube channel of approximately 200. The ultrafiltrate was chlorinated and then sent to a holding tank. Normally, the UF permeate collected in the holding tank until it was full, after which the UF unit was automatically shutoff by a tank level switch. When the level in the tank dropped a set amount the UF system was automatically reactivated.

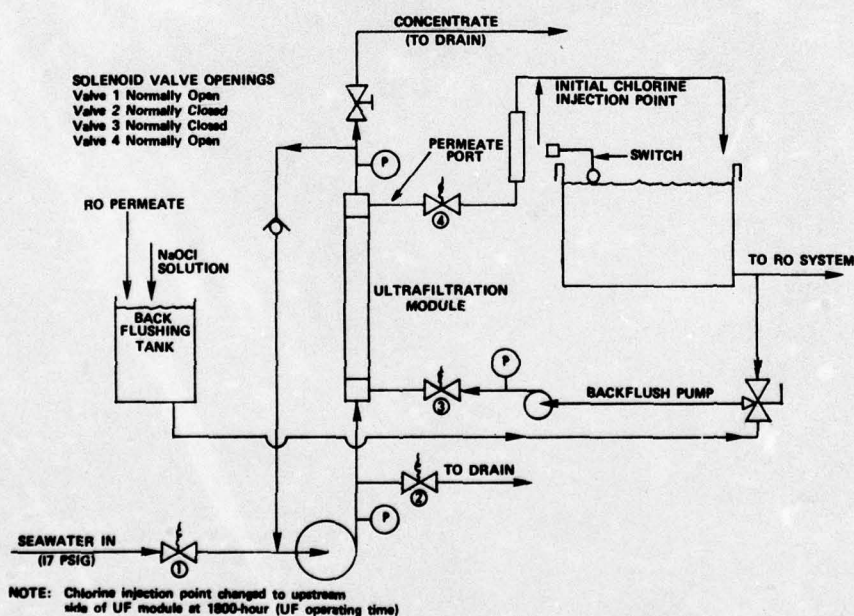


Figure 3-A  
Ultrafiltration System Used for the Pretreatment  
of Seawater



Backflushing was accomplished in two ways. First, each of the four solenoid valves was connected to a timer. Under normal operation, valves 1 and 4 were open. At every 2 hours of operation the timer would automatically shutoff valves 1 and 4 and the recirculation pump. At the same time, valves 2 and 3 were opened, and the backflush pump was turned on. UF permeate taken from the seawater holding tank was automatically pumped through valve 3, to the shell side of the module, through the membrane to the tube side, and then to the drain via valve 2.

The second method of backflushing was applied when the UF permeate rate had undergone a sizable decline. By this method, RO permeate and bleach were mixed in a separate tank to make a 300 ppm sodium hypochlorite solution. The timer was manually actuated to feed 10 gallons of chlorinated permeate to the UF module via valve 3.

### RESULTS

Figure 4-A gives the results of the UF system. Each point represents an average weekly value. As can be seen, two of the UF modules were replaced after their UF permeate quality dropped below their acceptable  $PI_{15}$  value limit. It was observed that with each UF module, the UF permeate quality decreased as the permeate rate increased slightly. This was evidence that the membrane surface was apparently being eroded thus increasing membrane porosity and decreasing filtration efficiency.

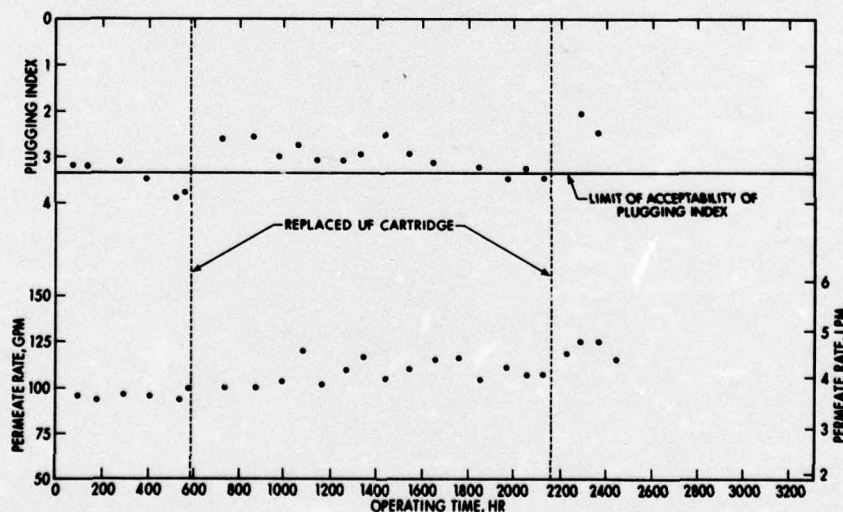


Figure 4-A  
Evaluation of UF on Wrightsville Beach Seawater

During the course of operation, individual UF permeate rates (not shown) declined 20% to 30% during periods of 50 to 70 hours. As was mentioned, the UF system automatically backflushed every 2 hours. It was hoped that this action would be sufficient to maintain stable permeate rates; however, the method of backflushing with chlorine was necessary to completely recover lost membrane flux rates.

#### CONCLUSIONS

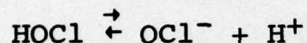
The effectiveness of UF for pretreatment of RO feedwater has clearly been demonstrated in this application. UF permeate  $PI_1$  values were acceptable, and the UF membrane product rate was generally stable. However, the high-frequency of UF module replacement due to UF permeate quality declines is seen to be the limiting factor in the usefulness of this method of filtration. The poor life of this pretreatment equipment would be a significant factor in the reliability of an overall RO desalination system and would therefore not be recommended for use at this time for shipboard application. Possibly, an initially tighter UF membrane would have improved operating life.



## APPENDIX B CHLORINE PROBE

Determining the level of chlorine in a given water stream is important in any freshwater production unit to monitor chlorine levels objectively and automate a chlorination system. Therefore, a chlorine probe and readout/control system was procured and placed in the test system. Eventually such a chlorine-monitoring system might be used to control the output of the electrolytic chlorinator to obtain a completely automated chlorination system.

As illustrated in item (b), figure 3 (of the text), the chlorine probe was placed in the permeate line to measure the permeate chlorine level. Each time a reading was taken, the chlorine level in the permeate was also checked by the orthotolodine method\* to compare the two levels of chlorine measurements. Hypochlorous acid in water partially ionizes to produce a mixture of itself and the hypochlorite and hydrogen ions as shown in the following reaction:



The reaction proceeds to the right under high pH conditions and to the left under low pH conditions. Under the high pH of natural seawater (7.8) only about 20% of the free chlorine is in the form of HOCl, while at the low pH of RO permeate (6.7) 80% of the free chlorine is in the form of HOCl. (For this reason the chlorine probe was initially placed in the permeate line.) The orthotolodine method measures the total concentration of free chlorine (HOCl and OCl<sup>-</sup>) and combined chlorine while the chlorine probe is designed to read only the hypochlorous acid (HOCl). Therefore, in any set of readings by the two methods of chlorine determination, the orthotolodine method would normally be expected to yield the higher values.

### RESULTS AND DISCUSSION

It was found that the chlorine level measured by the chlorine probe was consistently 20% greater than that reading taken by the orthotolodine test kit. These results, contrary to that which was expected, indicate that the chlorine probe was not properly standardized at the factory or that the orthotolodine test kit was

\*Orthotolodine Method for Water and Wastewater, APHA Standard Methods, 13th Edition, 117 (1971)

in error. (The orthotolodine method is, in fact, acknowledged as having considerable probability of error because it is temperature and time dependent as well as dependent upon individual interpretation of color comparison.) However, the important finding is that the chlorine probe did provide consistent readings throughout the test.



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